

Molecular double core-hole electron spectroscopy for chemical analysis

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(Dated: 20 April 2010)

We explore the potential of double core hole electron spectroscopy for chemical analysis in terms of x-ray two-photon photoelectron spectroscopy (XTPPS). The creation of deep single and double core vacancies induces significant reorganization of valence electrons. The corresponding relaxation energies and the interatomic relaxation energies are evaluated by CASSCF calculations. We propose a method how to experimentally extract these quantities by the measurement of single and double core-hole ionization potentials (IPs and DIPs). The influence of the chemical environment on these DIPs is also discussed for states with two holes at the same atomic site and states with two holes at two different atomic sites. Electron density difference between the ground and double core-hole states clearly shows the relaxations accompanying the double core-hole ionization. The effect is also compared with the sensitivity of single core hole ionization potentials (IPs) arising in single core hole electron spectroscopy. We have demonstrated the method for a representative set of small molecules LiF, BeO, BF, CO, N₂, C₂H₂, C₂H₄, C₂H₆, CO₂ and N₂O. The scalar relativistic effect on IPs and on DIPs are briefly addressed.

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I. INTRODUCTION

The effect of the chemical environment manifests itself in energy differences of molecular core levels with respect to the atomic ones referred to as "chemical shifts". These can be measured by core level spectroscopies, e.g., by x-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA) and by x-ray-induced Auger electron spectroscopy (XAES)¹. Both spectroscopies have shown to be exceedingly successful tools to reveal the quantitative elemental composition of molecules and solids.

More than two decades ago, Cederbaum et al.^{2,3} discovered that the creation of double core vacancies in molecular systems probes the chemical environment more sensitively than the creation of single core vacancies. Two-atomic site double ionization potentials, or briefly two-site DIPs (or two-site double ionization energies, DIES) are particularly sensitive to the chemical environment as the examples of the C_2H_2 , C_2H_4 , C_2H_6 ² and C_6H_6 ³ molecules demonstrate. The chemical shifts of one-atomic site DIPs, or briefly one-site DIPs, were found to be similar to the chemical shifts of the single core level ionization potentials (IPs), or ionization energies (IEs). This finding has given impetus to a number of theoretical studies aimed at elucidating properties of molecular double core hole states⁴⁻⁷.

So far experimental explorations of double core hole states with conventional XPS were restricted to those having two vacancies on the same atomic site only^{8,9} since the probability to produce a two-site double core hole state with one-photon absorption is practically zero at third-generation synchrotrons due to low x-ray intensities. This prevented further progress of the subject. The situation has changed with development of x-ray free-electron lasers (x-ray FELs)¹⁰. At FEL facilities in operations, such as FLASH in Hamburg¹¹ and SPring-8 Compact SASE Source (SCSS) test accelerator¹², multi-photon absorption processes resulting in multiply ionized states of various systems have been extensively studied¹³⁻¹⁷. In the x-ray FEL facility LCLS at SLAC National Accelerator Laboratory, which has just started operations¹⁸, ultrashort pulses of a duration about 1-fs containing 2.4×10^{11} photons with energies of 1 keV are expected to be generated^{19,20} thus opening up the possibility to study molecular two-site double core hole states. Inspired by the advent of the x-ray FEL at LCLS, Santra et al.²¹ have demonstrated theoretically by the proof-of-principle simulations on the organic para-aminophenol molecule that two-site double core hole states can indeed be probed by means of x-ray two-photon photoelectron spectroscopy (XTPPS).

The operating principle of XTPPS is depicted schematically in Fig. 1. The initial step in XTPPS corresponds conventional XPS, i.e., a neutral molecule with an energy E_0 is irradiated by an x-ray photon with an energy ω_X and a photoelectron with the kinetic energy $\vec{k}_{P,1}^2/2$ is ejected. This photoelectron carries information about a singly core ionized state E^+ of the molecule. If a second x-ray photon is absorbed before the intermediate core hole state decays, the second photoelectron expelled from the cation with the kinetic energy $\vec{k}_{P,2}^2/2$ carries information about a double ionization potential. It is important to have an intense x-ray pulse with a duration that is significantly shorter than the core-hole lifetimes (typical lifetimes of core ionized states of F, O, N and C atoms are 3 to 7 femtoseconds). If the pulse duration is longer than these lifetime, then Auger decay is likely to occur prior to absorbing the second photon and thus the double core hole states may not be probed. A dicationic state E^{++} of the system prepared by two-photon absorption decays electronically. Two primary Auger decays take place which overlap in time. An Auger decay happens preferably at that atomic site where the core hole has the shorter lifetime and an Auger electron with kinetic energy $\vec{k}_{A,1}^2/2$ is ejected. This process proceeds in the presence of the second core hole which also decays via the Auger mechanism emitting an electron with kinetic energy $\vec{k}_{A,2}^2/2$. The electrons ejected via such a cascade of Auger decays can in principle be measured by a novel Auger spectroscopy which we call x-ray two-photon-induced Auger electron spectroscopy (XTPAES).

It is worthwhile to note that double core ionization can be accompanied by various shake-up processes similar to single core ionization. These many-body effects should manifest themselves in XTPPS spectra as satellites which are of interest as well. Both x-ray two-photon-induced Auger spectra and satellites structures will be addressed elsewhere.

The subject of the present paper is the main double core hole states. In order to provide a guideline for XTPPS experiments, we have performed *ab initio* calculations of core level single and double ionization potentials of LiF, BeO, BF, CO, N₂, C₂H₂, C₂H₄, C₂H₆, CO₂, and N₂O molecules. In addition we have explored the sensitivity of the DIPs to the chemical environment of the core ionized atoms. We decompose the DIPs in three physical contributions such as the orbital energies, the electrostatic repulsion energy between two core holes and the generalized relaxation energy and describe how the latter can be extracted from the experimental XTPPS spectra.

II. COMPUTATIONAL METHODS

Ab initio calculations of the vertical ionization potentials of the single and double core vacancy states of LiF, BeO, BF, CO, N₂, C₂H₂, C₂H₄, C₂H₆, CO₂, and N₂O were performed using the Δ SCF²² and CASSCF²³ methods. The molecular geometries used in these calculations were optimized at the Møller-Plesset level of theory (MP2)²⁴ employing the correlation-consistent polarized valence triple zeta (cc-pVTZ) basis sets of Dunning²⁵. Depending on whether singly or doubly ionized states were considered, the configurations in the CASSCF method were restricted to those having one or two holes in the K-shell orbitals, respectively. We used the active spaces comprising all the occupied molecular orbitals (except for the 1s orbitals of the atoms other than H) and all the valence unoccupied π^* and σ^* ones which contain large contributions from different atomic *p* orbitals. Thus, the active space of the CASSCF calculations consists of 2s, σ , π , π^* and σ^* orbitals with core occupancy being fixed. The cc-pVTZ basis sets were employed in all the CASSCF and Δ SCF calculations. For CO and C₂H₂, the cc-pVDZ, cc-pCVTZ and cc-pVQZ basis sets were also used in order to examine the basis set dependence of our results. All the single and double core-hole states were solved by independent CASSCF calculations using different configuration space and, therefore, the calculated states are not strictly orthogonal to each other. However, the one and two-site double core-hole states are well separated in energy and their interaction are expected to be negligible.

For molecules with equivalent atoms, N₂, C₂H₂, C₂H₄, C₂H₆ and CO₂, we calculated double ionization potentials using both localized and delocalized molecular orbital pictures following the recipe given by Cederbaum et al.² and discuss differences between them. Note that only core orbitals were localized which was performed with the Boys method²⁶. In the localized representation we obtained the ionization potentials of the one-site double core hole states S_1^{-2} and S_2^{-2} as well as of the two-site double core hole states $S_1^{-1}S_2^{-1}$. Carrying out calculations with wave functions described by the linear combinations $S_1^{-2} \pm S_2^{-2}$ gives rise to double ionization potentials in the delocalized picture. Differences between single ionization potentials arising due to applying localized and delocalized representations are not studied in the present paper because they have been discussed in detail before^{27,28}.

In this work, we ignore the geometry relaxation of ionized state. In core ionization the change of geometry can be significant, depending on the case under investigation. In

single core ionization one can explain the measurements well by employing the concept of vertical transitions. As in single ionization, also in XTPPS where the two X-ray photons must be absorbed within a time shorter than the Auger decay times, the concept of vertical transitions can be expected to be very useful.

In order to assess the impact of scalar relativistic effects on the core level single and double ionization potentials we made relativistic CASSCF calculations for the CO and BF molecules using the eighth order Douglas-Kroll-Hess Hamiltonian (DKH8)^{29–33}. To get insight into the dynamic correlations, we also performed CI calculations with the CAS space plus single excitations from the CAS for both single and double core-hole states.

All calculations were done with the Molpro2008 quantum chemistry package³⁴.

III. RESULTS AND DISCUSSIONS

A. Single core hole states

Let us first discuss single core hole IPs. The ionization potential for the formation of a vacancy S^{-1} can be represented as

$$IP(S^{-1}) = -\varepsilon_S - RC(S^{-1}), \quad (1)$$

where ε_S is the corresponding orbital energy and $RC(S^{-1})$ is a contribution to the ionization potential due to relaxation $R(S^{-1})$ and correlation $C(S^{-1})$ effects:

$$RC(S^{-1}) = R(S^{-1}) + C(S^{-1}) \quad (2)$$

The relaxation and electron correlations intermix with each other and cannot be strictly separated. The separation of these quantities was discussed in details in a perturbative way³⁵ and in a nonperturbative way using MRCC³⁶. The correlation contribution can be further decomposed into two parts C1 and C2 (see Refs. 37 and 28) where C1 describes a part of the ground state pair correlation energy disappearing upon removal of an electron from the spin orbital S , and C2 accounts for changes in the remaining pair correlation energy due to relaxation. Except for C1 which is a very small contribution, all contributions to RC are thus associated with relaxation of molecular orbitals. Therefore, for brevity of discussion, we may call RC the generalized relaxation energy.

A straightforward way to obtain the relaxation energy is to perform Δ SCF calculations. $R(S^{-1})$ is then derived as the difference between the respective orbital energy (with opposite sign) and the calculated IP. In order to get a correlation contribution to IP, post-Hartree-Fock calculations are generally needed. CASSCF is one of these methods. Noteworthy, in systems with core holes delocalized due to symmetry requirements, C2 can be accounted by performing Δ SCF calculations using localized orbitals instead of delocalized ones as shown by Cederbaum and Domcke²⁸.

In Table I we list IPs calculated with the CASSCF and Δ SCF methods together with available experimental values^{38–44}. Table I also contains the constituting parts of IPs, namely the orbital energies, the relaxation energies obtained from Δ SCF calculations, as well as the generalized relaxation and pure correlation contributions, both obtained from CASSCF calculations. The correlation contributions were calculated by subtracting the CASSCF IPs from the Δ SCF ones. Note that, since Δ SCF calculations for molecules with equivalent atoms were performed using the localized representation, the calculated IPs correspond to the localized $1s$ orbitals rather than to the delocalized $1\sigma_g$ and $1\sigma_u$.

In general, the agreement between the CASSCF and experimental results is reasonable. This concerns both the absolute values of IPs and the g-u energy splittings for molecules with equivalent atoms. Except for basis set effects which always are an issue in *ab initio* calculations, and relativistic effects, deviations from the experiment are attributed to the lack of dynamic correlations in the ground and single core hole states, and to the core-valence separation approximation employed in the calculations. We notice that influences of the above-mentioned effects and approximations partially compensate for each other. Indeed, performing calculations without core-valence separability lowers IPs⁴⁵. A lowering of IPs can also be achieved by improving basis sets. On the other hand, taking into account relativistic effects increases IPs. In Appendices A and B we explore the basis sets and relativistic effects in more detail.

It is interesting to compare the different contributions to IPs in Eq. (1). After the orbital energy, the relaxation energy represents the largest constituent part of a core level IP. It increases nearly proportional to the atomic number Z . For some molecules, however, remarkable deviations from this trend occur under influence of the chemical environment. A crucial role for the relaxation energy plays the change of the electron density distribution of valence electrons, $\Delta\rho$, in an atom due to a formation of chemical bonds with neighbors,

and the interaction of $\Delta\rho$ with the core hole. Ionic bonds give rise to the strongest changes of the electron density distribution. As a consequence, the relaxation energies associated with core ionization of electron acceptors in ionic molecules (e.g. O and F in BeO and LiF, respectively) are noticeably larger than the relaxation energies of the same atoms bound by covalent bonds with their neighbors (O and F in CO and BF, respectively). For other factors influencing the relaxation energies see Ref. 2.

In comparison to relaxation effects, correlation effects induced by core ionization are rather small. According to our calculations, the magnitude of the static correlation effects does not exceed 3 eV for the molecules studied and accounting for missing dynamic correlation can hardly modify this situation dramatically. Interestingly, the largest correlation effects manifest themselves in atoms whose neighbors are the strong electron acceptors O and F.

The effect of the chemical environment on core level ionization potentials of various systems including the molecules explored here is rather well established and we therefore refrain from long discussions on this subject. We only mention that the chemical environment is able to introduce large changes in the ionization potentials as, for example, can be realized by comparing molecules with ionic and covalent bonds. On the other hand, in the sequence of the C_2H_2 , C_2H_4 , C_2H_6 molecules characterized by the triple, double and single carbon-carbon bond, respectively, the impact of the chemical environment is rather moderate. In contrast to single core hole ionization potentials, double core hole ionization potentials reveal much more pronounced sensitivity to the chemical environment as it was first demonstrated in Refs. 2 and 3.

B. Double core hole states

1. General equations and results

In analogy to Eq. (1), we represent the double ionization potential of a state with two core vacancies S_i^{-1} and S_j^{-1} as

$$DIP(S_i^{-1}, S_j^{-1}) = -\varepsilon_{S_i} - \varepsilon_{S_j} - RC(S_i^{-1}, S_j^{-1}) + E_{RE}, \quad (3)$$

where E_{RE} is the repulsion-exchange energy of the two core holes. For an one-site double core hole state, it is described by the two-electron integral $V_{S_i S_i S_i S_i}$, or $(S_i S_i | S_i S_i)$, and,

for a two-site double core hole state, by a linear combination of the integrals $V_{S_i S_j S_i S_j}$ and $V_{S_i S_j S_j S_i}$ where the exchange term is negligibly small when the core holes are well localized⁵.

The generalized relaxation $RC(S_i^{-1}, S_j^{-1})$ can be decomposed into three parts

$$RC(S_i^{-1}, S_j^{-1}) = RC(S_i^{-1}) + RC(S_j^{-1}) + NRC(S_i^{-1}, S_j^{-1}), \quad (4)$$

where $RC(S_i^{-1})$ given by Eq. (2) describes relaxation and correlation effects induced by creation of the core vacancy S_i^{-1} as there were no core vacancy S_j^{-1} . The relaxation and correlation energies are expected to be non-additive upon creation of multiple vacancies. A possible deviation from additivity is thus described in Eq. (4) by the *non-additivity* term $NRC(S_i^{-1}, S_j^{-1})$.

Depending on whether two core holes were created on the same atomic site or on different atomic sites, $NRC(S_i^{-1}, S_j^{-1})$ may be called the *excess* generalized relaxation energy, $ERC(S_i^{-1}, S_i^{-1})$, or the *interatomic* generalized relaxation energy, $IRC(S_i^{-1}, S_j^{-1})$. Note that, while the $RC(S_i^{-1})$ and $ERC(S_i^{-1}, S_i^{-1})$ measure local properties of a core ionized atom, $IRC(S_i^{-1}, S_j^{-1})$ measures the impact of the environment "between" the atoms involved.

In Table II we list the calculated double ionization potentials. We also show the correlation contributions to DIPs. As one can see these contributions are remarkably larger than those to the single IPs and may constitute 5.6 eV. In the special cases, however, when we performed calculations with delocalized core orbitals, differences between Δ SCF and CASSCF values rise to 27-35 eV resulting from the failure of the Δ SCF method in the delocalized picture to account for all relaxation contributions as described by Cederbaum et al.^{2,3}.

One can notice by comparing Table I and II that the impact of the chemical environment is different for double and single ionization potentials. Of particular interest is to compare two-site DIPs with single IPs since their sensitivities to the chemical environment reveal major differences. A prominent example already discussed in detail in Ref. 2 is the hydrocarbons C_2H_2 , C_2H_4 and C_2H_6 . Here, the chemical shifts in the two-site DIPs are much more pronounced than in the single IPs being also attributed to different carbon-carbon bondlengths resulted from a different number of hydrogen atoms in these molecules. In XPS one can hardly distinguish between these three compounds while in XTPPS this should be possible in principle. The situation is somewhat different for the individual molecule N_2O . In this molecule the sensitivity of two-site DIPs to the chemical environment is lower

compared to that of single IPs. Indeed, the core ionization potentials of the terminal and central nitrogen atoms differ by 4 eV whereas the difference between the $N_t 1s^{-1} O 1s^{-1}$ and $N_c 1s^{-1} O 1s^{-1}$ double ionization potentials constitutes 2.3-2.8 eV. The latter energy difference is much lower than 11 eV which one would expect taking into account only the differences between the $N_c O$ and $N_t O$ bondlengths and between the single core hole ionization potentials. As we show below, the reason for such a dramatic reduction of the chemical shift has to do with distinct relaxation processes induced by the creation of different pairs of core holes.

Taking into account Eqs. (1) and (4), we can represent $DIP(S_i^{-1}, S_j^{-1})$ as

$$DIP(S_i^{-1}, S_j^{-1}) = IP(S_i^{-1}) + IP(S_j^{-1}) - NRC(S_i^{-1}, S_j^{-1}) + E_{RE}, \quad (5)$$

and define the ionization potential of the core vacancy S_i^{-1} in the presence of the core vacancy S_j^{-1} as

$$IP(S_j^{-1}; S_i^{-1}) = IP(S_i^{-1}) - NRC(S_i^{-1}, S_j^{-1}) + E_{RE}, \quad (6)$$

whereas

$$IP(S_i^{-1}; S_j^{-1}) = IP(S_j^{-1}) - NRC(S_i^{-1}, S_j^{-1}) + E_{RE} \quad (7)$$

is defined as the ionization potential of the core vacancy S_j^{-1} in the presence of the core vacancy S_i^{-1} .

Both the ionization potentials $IP(S_i^{-1})$ of a neutral system and the ionization potentials $IP(S_i^{-1}; S_j^{-1})$ of a core-ionized one can be obtained experimentally, e.g., by means of XTPPS. In XTPPS, the kinetic energy $KE(S_i^{-1})$ of the first photoelectron ejected from the orbital S_i defines $IP(S_i^{-1})$, whereas the kinetic energy $KE(S_i^{-1}; S_j^{-1})$ of the second photoelectron ejected from the orbital S_j defines $IP(S_i^{-1}; S_j^{-1})$. Obviously, the sum $IP(S_i^{-1}) + IP(S_i^{-1}; S_j^{-1})$ gives $DIP(S_i^{-1}, S_j^{-1})$. As shown below, important properties of the system under study can be extracted also from the measurable energy difference

$$\begin{aligned} \Delta E &= KE(S_i^{-1}) - KE(S_j^{-1}; S_i^{-1}) = IP(S_j^{-1}; S_i^{-1}) - IP(S_i^{-1}) \\ &= DIP(S_j^{-1}, S_i^{-1}) - IP(S_i^{-1}) - IP(S_j^{-1}). \end{aligned} \quad (8)$$

Similar to $DIP(S_i^{-1}, S_j^{-1})$, the kinetic energy $KE(S_i^{-1}; S_j^{-1})$ depends significantly on the mutual arrangement of the core vacancies S_j^{-1} and S_i^{-1} in a molecule. This is clearly

seen from Table III where we collect the kinetic energies of all the core electrons of the CO molecule which one would detect in an XTPPS experiment given that the molecule is irradiated by an x-ray pulse with photon energies of 1 keV. First of all, we notice that it is more difficult to remove an electron from the core ionized CO molecule than from the neutral one. The respective energy difference is about 70-90 eV when the first and the second core electrons are ejected from the same core orbital. This energy difference reduces drastically to about 15 eV when different core orbitals are affected. Apparently, the electrostatic interaction between the two core holes plays a crucial role here. $NRC(S_i^{-1}, S_j^{-1})$ exerts an influence on the above energy differences too, as can be deduced from Eqs. (6) and (7).

2. *One-site double core hole states*

If $S_i = S_j = S$ then ΔE takes the form

$$\Delta E1(S^{-2}) = -ERC(S^{-1}, S^{-1}) + V_{SSSS}. \quad (9)$$

We calculated $\Delta E1(S^{-2})$ for the molecules under study using the respective CASSCF single and double core hole ionization potentials and collect them in Table IV. The dependence of $\Delta E1(S^{-2})$ on the atomic number Z is displayed in Fig. 2(a).

The excess generalized relaxation energy $ERC(S^{-1}, S^{-1})$ can be easily obtained by measuring the energy difference $\Delta E1(S^{-2})$ provided that the integral V_{SSSS} is known. V_{SSSS} can be extracted from *ab initio* Hartree-Fock calculations on the electronic ground state of neutral molecules. Alternatively, it can be calculated by using the approximate analytical expression suggested in Ref. 2 :

$$V_{SSSS} = (2^{5/2}/3\pi)(Z - 2^{-3/2}). \quad (10)$$

The respective results for V_{SSSS} and a difference between them are discussed in Appendix C.

Using Eq. (4) we represent $ERC(S^{-1}, S^{-1})$ as

$$ERC(S^{-1}, S^{-1}) = RC(S^{-1}, S^{-1}) - 2RC(S^{-1}). \quad (11)$$

It has been shown in Ref. 2 that at the second order perturbation theory the following relationship between the relaxation energies is valid:

$$R(S^{-1}, S^{-1}) = 4R(S^{-1}). \quad (12)$$

Since the impact of correlation into ionization potentials is small compared to the impact of relaxation, we expect that a similar relationship exists between the generalized relaxation energies $RC(S^{-1}, S^{-1})$ and $RC(S^{-1})$. Let us therefore introduce that

$$RC(S^{-1}, S^{-1}) = n \times RC(S^{-1}), \quad (13)$$

and find the optimal n . After the substitution of Eqs. (11) and (13) into (9), we get

$$\Delta E1(S^{-2}) = -(n - 2)RC(S^{-1}) + V_{SSSS}. \quad (14)$$

Now we can easily calculate n by using the *ab initio* results for $\Delta E1$, RC and V_{SSSS} . The respective values of n as a function of the atomic number Z are shown in Fig. 3. As one can see, deviations of the calculated n from the expected value of 4 are rather small (15% in the worst case of Li) and therefore $n = 4$ can be considered as a plausible approximation for the molecules studied in the present work.

As a result, we obtain the following expression for the generalized relaxation energy:

$$RC(S^{-1}) = (V_{SSSS} - \Delta E1(S^{-2}))/2. \quad (15)$$

The values of $RC(S^{-1})$ calculated by means of Eq. (15) are given in Table IV and also plotted in Fig. 2(b) as a function of Z . It is worthwhile to note a reasonable agreement between them and the corresponding results from Table I.

3. *Two-site double core hole states*

If $S_i \neq S_j$ then ΔE takes the form

$$\Delta E2(S_i^{-1}, S_j^{-1}) = -IRC(S_i^{-1}, S_j^{-1}) + 1/r, \quad (16)$$

where the repulsion-exchange energy E_{RE} has been approximated by the inverse of the distance r between the two atoms with the core vacancies S_i^{-1} and S_j^{-1} . We calculated $\Delta E2(S_i^{-1}, S_j^{-1})$ using the CASSCF double and single core hole ionization potentials and collected these results in Table IV.

By looking at Eq. (16), one expects a linear dependence between $\Delta E2(S_i^{-1}, S_j^{-1})$ and $1/r$. This expectation is not realized however as seen from Fig. 4(a) where a variation of $\Delta E2$ with $1/r$ is shown. To elucidate the complex behavior of $\Delta E2$ we calculated the interatomic generalized relaxation energy $IRC(S_i^{-1}, S_j^{-1})$ from Eq. (16) and plotted these

results as a function of r in Fig. 4(b). We found both positive and negative values of IRC (see also Table IV) which indicate on an enhancement or suppression of relaxation effects, respectively.

In the case of diatomic molecules, IRC is always negative and thus the relaxation is suppressed. This suppression may be interpreted by considering the change of the electron density. A core hole S_i^{-1} attracts valence electrons and increases the electron density in its vicinity, yielding a deficiency of the electron density in the vicinity of the atom with a core orbital S_j . The relaxation energy corresponding to the creation of the core vacancy S_j^{-1} in the presence of the core hole S_i^{-1} is therefore reduced. The amplitudes of IRC are smaller for LiF, BF, and N₂ than for BeO, and CO. This is because the electrons are strongly attracted to the F site in LiF and BF, or tightened in the triple bond in N₂ and thus the electron density flow due to core hole creation is suppressed by these chemical environments.

Values of $IRC(S_i^{-1}, S_j^{-1})$ for the polyatomic molecules C₂H₂, C₂H₄, and C₂H₆ are, in contrast, positive. The enhancement of the relaxation for these molecules occurs due to the electron density flowing from the C-H bonds to the two carbon core hole sites.

The interatomic generalized relaxation energy exhibits a very interesting behavior with r in triatomic molecules as seen from Fig. 4(b). $IRC(S_i^{-1}, S_j^{-1})$ is positive for CO₂ and N₂O when S_i^{-1} and S_j^{-1} are in adjacent atoms, namely in C and O in CO₂ and in N_t and N_c or in N_c and O in N_tN_cO. In these cases, the third atom plays the role of an electron donor and enhances the relaxation of the double core hole in the other two sites. The values of IRC are, on the other hand, negative for CO₂ and N₂O with two holes in the terminal atoms, namely with holes in the two O sites of CO₂ and with holes in the N_t and O sites of N₂O. In these cases, the creation of the core hole on one site already withdraws the electron density from the central atom and thus reduces the possibility of relaxation due to the creation of the second hole in the other terminal site.

In order to analyze the reorganization caused by double core hole ionization, we calculated the electron density difference between the ground and double core hole ionized states. These electron density differences without the 1s contribution are plotted in Fig. 5, to better visualize the reorganization of the valence electrons. In the blue or green region, the electron density increases, while the density decreases in the red region. In the C₁1s⁻² state of C₂H₄, the electron density of the C₁-C₂, C₁-H bond and H atoms connected to C₁ atom reduces and flows to the region around C₁ atom as shown in Fig. 5(a). In the C₁1s⁻¹C₂1s⁻¹

state of C_2H_4 , on the other hand, the electron density in the region of C-H bonds and H atoms flows to the region of both C atoms as in Fig. 5(b). This explains the positive value of IRC in the $\text{C}_11s^{-1}\text{C}_21s^{-1}$ state as noted above. In the case of the $\text{O}1s^{-2}$ state of CO, the electron density of the CO bond is used for the reorganization around the O atom (Fig. 5(c)).

IV. CONCLUSIONS

We have computed the ionization potentials of single and double core hole states of the small molecules LiF, BeO, BF, CO, N_2 , C_2H_2 , C_2H_4 , C_2H_6 , CO_2 , and N_2O by means of the ΔSCF and CASSCF methods in order to explore the impact of the chemical environment on the respective ionization processes and provide a guidance for x-ray two-photon photoelectron spectroscopy (XTPPS) experiments.

Our calculations have demonstrated that except for N_2O , the double ionization potentials, especially the two-site ones of all these molecules are more sensitive to the chemical environment than the single ionization potentials. The sensitivity to the chemical environment of the two-site DIPs of N_2O is mainly governed by the interatomic relaxation energies which, in turn, strongly depend on the electron density distribution between the core-ionized atoms.

The quantities extracted from XTPPS are differences between the kinetic energies of core electrons ejected via the first and second ionization steps, i.e., of core electrons ejected from neutral and core-ionized systems, respectively. These kinetic energy differences are defined by a localization of the two core vacancies created and by relaxation processes induced by double core ionization. We have shown how one can extract the generalized relaxation energy associated with single core ionization as well as the excess and interatomic generalized relaxation energies associated with one-site and two-site double core ionizations, respectively, from experimental data by knowing the repulsion energy between the two core holes. The corresponding XTPPS experiments are now in preparation in the x-ray free electron laser facility LCLS at SLAC National Accelerator Laboratory.

ACKNOWLEDGMENTS

M.E. acknowledges the support from JST-CREST and a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science, the Next Generation Supercomputing Project, and the Molecular-Based New Computational Science Program, NINS. H.F. and K.U. acknowledge the support for the X-ray Free Electron Laser Utilization Research Project of Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT). C.B. was supported by National Science Foundation under the grants No PHY-0701372 and No PHY-0449235. The Heidelberg group is grateful for financial support by the Deutsche Forschungsgemeinschaft. The computations were partly performed using the Research Center for Computational Science, Okazaki, Japan.

Appendix A: Scalar relativistic effects

It is essential in view of their large impact to take into account relativistic effects when considering systems with heavy atoms. For light atoms, relativistic effects are of less importance but still should be accounted when highly accurate results are needed. In the present work we assess the impact of scalar relativistic effects on IPs and DIPs by carrying out calculations with the relativistic DKH8 Hamiltonian for the CO and BF molecules. The results of these calculations are shown in Table V. As one can see the magnitude of the scalar relativistic effects on the single ionization potentials grows with the increasing atomic mass constituting 0.03, 0.09, 0.35, and 0.59 eV in the case of the B, C, O and F atoms, respectively. One of us has shown that a similar tendency is observed also for the third-row Si, P, S, Cl atoms⁴⁶. A growth of scalar relativistic effects with the atomic mass exhibits also in the case of double core hole ionization. We note that the relativistic effects on the one-site DIPs are about 2.3-3 times larger than those on the respective single IPs. Interestingly that in the case of two-site doubly ionized states the relativistic effects are perfectly described by the sum of the relativistic effects associated with the constituting single core vacancies.

Appendix B: Basis set effects

In this section we explore the basis set dependence of the single and double core hole ionization potentials by examples of the C₂H₂ and CO molecules. We have examined four

basis sets: the Dunning’s correlation-consistent basis sets cc-pVXZ (X=D,T,Q) and the cc-pCVTZ one. The latter contains tight basis functions which are added for a better description of properties of core-level states. The results are collected in Table VI. By looking at the sequence of the cc-pVXZ results we find significant differences between the cc-pVDZ and cc-pVQZ values, especially in the case of the one-site DIPs where differences of nearly 10 eV are present. The major changes occur upon improving the basis set from a double- to triple-zeta quality. Choosing the cc-pVQZ basis sets lowers ionization potentials by only 0.2-1.2 eV relative to the cc-pVTZ values. The cc-pCVTZ results are lower in energy than the cc-pVTZ ones whereby they nearly coincide with the cc-pVQZ results in the case of the CO molecule. We used the cc-pVTZ basis throughout as a compromise between the accuracy of the results and the computational costs. For the double core-hole states, the relaxation of valence orbitals is important, in particular for the one-site states where all 1s electrons on one atom are missing.

Appendix C: Evaluation of the V_{SSSS} integral

The approximate analytical expression (10) was proposed in Ref. 2 for the two electron integral V_{SSSS} . By comparing the analytical results with the explicit *ab initio* ones (dotted curve and filled circles in Fig. 6, respectively) we found a progressively growing deviation between them with increasing Z (1.5 eV for lithium, 4.5 eV for fluorine). This deviation can be removed by substituting $1.037 \cdot Z$ instead of Z in Eq. (10), where the coefficient 1.037 has been extracted from a linear fit (dashed curve in Fig. 6) of the *ab initio* results.

Appendix D: Effect of dynamic correlations

We performed the CI calculations with the space of the singly excited configurations from the CASSCF configurations and examined the semi-internal correlation. The results for the single and double core-hole states of C_2H_2 and CO were summarized in Table VII. The difference between the results of CI and CASSCF provides the effect of the semi-internal correlation. The semi-internal correlation has small effect on IPs of the single hole states, less than +0.03 eV for $C1s^{-1}$ and +0.25 eV for $O1s^{-1}$. The effect for the one-site double core-hole states is significant as $+0.24 \sim +0.54$ eV, while it is small for the two-site double

core-hole states as $+0.08 \sim +0.12$ eV.

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TABLE I. Single core hole ionization potentials and their constituent parts (in eV) as calculated with the Δ SCF and CASSCF methods. Experimental values of the ionization potentials, where available, taken from Refs. 38-44 are also shown. The cc-pVTZ basis sets were employed.

Molecule	Core level,	$-\varepsilon_S$	Δ SCF		CASSCF			Expt.
	S		IP	$R(S^{-1})$	IP	$RC(S^{-1})$	$C(S^{-1})$	
LiF	Li1s	66.407	65.460	0.947	65.334	1.073	0.126	
	F1s	710.484	688.187	22.297	688.044	22.440	0.143	
BeO	Be1s	128.383	124.406	3.977	123.399	4.984	1.007	
	O1s	556.694	535.181	21.513	535.075	21.619	0.106	
BF	B1s	209.735	202.539	7.196	201.724	8.011	0.815	
	F1s	717.810	695.873	21.937	695.915	21.895	-0.042	
CO	C1s	309.111	298.256	10.855	296.358	12.753	1.898	296.069
	O1s	562.348	542.801	19.547	542.820	19.528	-0.019	542.543
N ₂ O	N _t 1s	427.159	409.615	17.544	408.614	18.545	1.001	408.5
	N _c 1s	432.005	415.373	16.632	412.524	19.481	2.849	412.5
	O1s	563.760	543.046	20.714	542.537	21.223	0.509	542.0
CO ₂	C1s	311.930	300.607	11.323	297.647	14.283	2.960	296.78
	O1g	561.956	541.979	19.977	542.870	19.086	-0.891	540.6
	O1u	561.954		19.975	542.868	19.086	-0.889	
C ₂ H ₂	C1g	305.897	292.535	13.362	292.202	14.062	0.700	291.14, 291.20
	C1u	305.794		13.259	292.111	14.054	0.795	
C ₂ H ₄	C1g	305.557	291.801	13.756	291.344	14.213	0.457	290.70, 290.88
	C1u	305.508		13.707	291.297	14.211	0.504	
C ₂ H ₆	C1g	305.040	291.774	13.266	291.147	13.893	0.627	290.76, 290.74
	C1u	305.023		13.249	291.125	13.898	0.649	
N ₂	N1g	426.686	411.242	15.444	411.027	15.659	0.215	409.93
	N1u	426.588		15.346	410.932	15.656	0.310	409.82

TABLE II. Calculated double core hole ionization potentials and the static correlation energies C (in eV). T and S refer to triplet and singlet couplings of two core holes created on different atomic sites, respectively. The cc-pVTZ basis sets were employed.

Molecule	Core level	Δ SCF	CASSCF	
		DIP	DIP	C
LiF	Li1s ⁻²	173.125	172.595	0.530
	F1s ⁻²	1480.418	1481.495	-1.077
	Li1s ⁻¹ F1s ⁻¹ , S	763.447	763.211	0.236
	Li1s ⁻¹ F1s ⁻¹ , T	763.443	763.277	0.166
BeO	Be1s ⁻²	300.585	298.032	2.553
	O1s ⁻²	1158.135	1159.351	-1.216
	Be1s ⁻¹ O1s ⁻¹ , S	672.823	671.801	1.022
	Be1s ⁻¹ O1s ⁻¹ , T	672.823	672.128	0.695
BF	B1s ⁻²	468.243	465.323	2.920
	F1s ⁻²	1494.930	1495.809	-0.879
	B1s ⁻¹ F1s ⁻¹ , S	910.946	910.568	0.378
	B1s ⁻¹ F1s ⁻¹ , T	910.946	910.678	0.268
CO	C1s ⁻²	667.902	664.418	3.484
	O1s ⁻²	1175.376	1176.561	-1.185
	C1s ⁻¹ O1s ⁻¹ , S	857.072	854.743	2.329
	C1s ⁻¹ O1s ⁻¹ , T	857.072	855.200	1.872
N ₂ O	N _t 1s ⁻²	894.485	893.926	0.559
	N _c 1s ⁻²	906.773	902.312	4.461
	O1s ⁻²	1173.683	1173.249	0.434
	N _t 1s ⁻¹ N _c 1s ⁻¹ , S	838.282	832.962	5.320
	N _t 1s ⁻¹ N _c 1s ⁻¹ , T	838.279	833.215	5.064
	N _t 1s ⁻¹ O1s ⁻¹ , S	965.806	963.041	2.765
	N _t 1s ⁻¹ O1s ⁻¹ , T	965.806	963.266	2.540
	N _c 1s ⁻¹ O1s ⁻¹ , S	968.082	965.793	2.289
	N _c 1s ⁻¹ O1s ⁻¹ , T	968.082	965.623	2.459

CO ₂	C1s ⁻²	670.280	664.629	5.651
	O1s ⁻²	1172.821	1171.909	0.912
	C1s ⁻¹ O1s ⁻¹ , S	854.682	851.059	3.623
	C1s ⁻¹ O1s ⁻¹ , T	854.682	851.199	3.483
	O1s ⁻¹ O2s ⁻¹ , S	1094.795	1094.090	0.705
	O1s ⁻¹ O2s ⁻¹ , T	1094.795	1094.167	0.628
C ₂ H ₂	C1s ⁻²	651.265	650.228	1.037
	C2s ⁻²	651.265	650.228	1.037
	C1s ⁻¹ C2s ⁻¹ , S	598.281	594.590	3.691
	C1s ⁻¹ C2s ⁻¹ , T	598.281	595.197	3.084
	C1s ⁻² -C2s ⁻²	681.646	651.334	30.312
	C1s ⁻² +C2s ⁻²	681.646	651.334	30.312
C ₂ H ₄	C1s ⁻²	648.964	648.556	0.408
	C2s ⁻²	648.964	648.556	0.408
	C1s ⁻¹ C2s ⁻¹ , S	594.850	591.514	3.336
	C1s ⁻¹ C2s ⁻¹ , T	594.850	591.956	2.894
	C1s ⁻² -C2s ⁻²	679.386	649.703	29.683
	C1s ⁻² +C2s ⁻²	679.386	649.703	29.683
C ₂ H ₆	C1s ⁻²	649.714	648.827	0.887
	C2s ⁻²	649.714	648.827	0.887
	C1s ⁻¹ C2s ⁻¹ , S	591.447	589.007	2.440
	C1s ⁻¹ C2s ⁻¹ , T	591.447	589.192	2.255
	C1s ⁻² -C2s ⁻²	677.339	649.898	27.441
	C1s ⁻² +C2s ⁻²	677.339	649.898	27.441
N ₂	N1s ⁻²	901.704	901.155	0.549
	N2s ⁻²	901.704	901.155	0.549
	N1s ⁻¹ N2s ⁻¹ , S	839.912	835.784	4.128
	N1s ⁻¹ N2s ⁻¹ , T	839.912	836.437	3.475
	N1s ⁻² -N2s ⁻²	938.943	903.727	35.216
	N1s ⁻² +N2s ⁻²	938.943	903.727	35.216

TABLE III. Kinetic energies of photoelectrons one would detect in an XTPPS experiment by irradiating the CO molecule with an x-ray pulse with photon energies of 1 keV. The sequence of the core vacancies in the records reflects the sequence of ionization steps. T and S refer to triplet and singlet couplings of two core holes created on different atomic sites, respectively.

State	KE (eV)
C1s^{-1}	703.642
$\text{C1s}^{-1}\text{C1s}^{-1}$	631.940
$\text{O1s}^{-1}\text{C1s}^{-1}$, S	688.077
$\text{O1s}^{-1}\text{C1s}^{-1}$ T	687.620
O1s^{-1}	457.180
$\text{O1s}^{-1}\text{O1s}^{-1}$	366.259
$\text{C1s}^{-1}\text{O1s}^{-1}$, S	441.615
$\text{C1s}^{-1}\text{O1s}^{-1}$, T	441.518

TABLE IV. Calculated energy differences $\Delta E1(S_i^{-2})$ and $\Delta E2(S_i^{-1}, S_j^{-1})$ together with the intra- and interatomic generalized relaxation energies $RC(S_i^{-1})$ and $IRC(S_i^{-1}, S_j^{-1})$ (in eV).

Molecule	Energy difference		Generalized relaxation energy	
LiF	$\Delta E1(\text{Li}1s^{-2})$	41.927	$RC(\text{Li}1s^{-1})$	1.41
	$\Delta E1(\text{F}1s^{-2})$	105.407	$RC(\text{F}1s^{-1})$	20.17
	$\Delta E2(\text{Li}1s^{-1}, \text{F}1s^{-1})$	9.833	$IRC(\text{Li}1s^{-1}, \text{F}1s^{-1})$	-0.74
BeO	$\Delta E1(\text{Be}1s^{-2})$	51.234	$RC(\text{Be}1s^{-1})$	5.23
	$\Delta E1(\text{O}1s^{-2})$	89.201	$RC(\text{O}1s^{-1})$	19.90
	$\Delta E2(\text{Be}1s^{-1}, \text{O}1s^{-1})$	13.327	$IRC(\text{Be}1s^{-1}, \text{O}1s^{-1})$	-2.69
BF	$\Delta E1(\text{B}1s^{-2})$	61.875	$RC(\text{B}1s^{-1})$	8.38
	$\Delta E1(\text{F}1s^{-2})$	103.979	$RC(\text{F}1s^{-1})$	20.88
	$\Delta E2(\text{B}1s^{-1}, \text{F}1s^{-1})$	12.929	$IRC(\text{B}1s^{-1}, \text{F}1s^{-1})$	-1.52
CO	$\Delta E1(\text{C}1s^{-2})$	71.702	$RC(\text{C}1s^{-1})$	11.87
	$\Delta E1(\text{O}1s^{-2})$	90.921	$RC(\text{O}1s^{-1})$	19.03
	$\Delta E2(\text{C}1s^{-1}, \text{O}1s^{-1})$	15.565	$IRC(\text{C}1s^{-1}, \text{O}1s^{-1})$	-2.80
N ₂	$\Delta E1(\text{N}1s^{-2})$	79.196	$RC(\text{N}1s^{-1})$	17.65
	$\Delta E2(\text{N}_1 1s^{-1}, \text{N}_2 1s^{-1})$	13.825	$IRC(\text{N}_1 1s^{-1}, \text{N}_2 1s^{-1})$	-0.65
C ₂ H ₂	$\Delta E1(\text{C}1s^{-2})$	66.653	$RC(\text{C}1s^{-1})$	15.06
	$\Delta E2(\text{C}_1 1s^{-1}, \text{C}_2 1s^{-1})$	11.015	$IRC(\text{C}_1 1s^{-1}, \text{C}_2 1s^{-1})$	0.96
C ₂ H ₄	$\Delta E1(\text{C}1s^{-2})$	65.915	$RC(\text{C}1s^{-1})$	15.42
	$\Delta E2(\text{C}_1 1s^{-1}, \text{C}_2 1s^{-1})$	8.873	$IRC(\text{C}_1 1s^{-1}, \text{C}_2 1s^{-1})$	1.94
C ₂ H ₆	$\Delta E1(\text{C}1s^{-2})$	66.555	$RC(\text{C}1s^{-1})$	15.06
	$\Delta E2(\text{C}_1 1s^{-1}, \text{C}_2 1s^{-1})$	6.735	$IRC(\text{C}_1 1s^{-1}, \text{C}_2 1s^{-1})$	2.72
CO ₂	$\Delta E1(\text{C}1s^{-2})$	69.335	$RC(\text{C}1s^{-1})$	13.76
	$\Delta E1(\text{O}1s^{-2})$	86.171	$RC(\text{O}1s^{-1})$	22.70
	$\Delta E2(\text{C}1s^{-1}, \text{O}1s^{-1})$	10.572	$IRC(\text{C}1s^{-1}, \text{O}1s^{-1})$	1.79
	$\Delta E2(\text{O}1s^{-1}, \text{O}1s^{-1})$	8.352	$IRC(\text{O}1s^{-1}, \text{O}1s^{-1})$	-2.19
N ₂ O	$\Delta E1(\text{N}_t 1s^{-2})$	76.698	$RC(\text{N}_t 1s^{-1})$	17.78
	$\Delta E1(\text{N}_c 1s^{-2})$	77.264	$RC(\text{N}_c 1s^{-1})$	17.47
	$\Delta E1(\text{O}1s^{-2})$	88.175	$RC(\text{O}1s^{-1})$	20.40
	$\Delta E2(\text{N}_t 1s^{-1}, \text{N}_c 1s^{-1})$	11.827	$IRC(\text{N}_t 1s^{-1}, \text{N}_c 1s^{-1})$	1.11
	$\Delta E2(\text{N}_t 1s^{-1}, \text{O}1s^{-1})$	20.732	$IRC(\text{N}_t 1s^{-1}, \text{O}1s^{-1})$	0.07
	$\Delta E2(\text{N}_c 1s^{-1}, \text{O}1s^{-1})$	11.890	$IRC(\text{N}_c 1s^{-1}, \text{O}1s^{-1})$	-6.00

TABLE V. Single and double core hole ionization potentials of CO and BF calculated with the CASSCF method using the relativistic DKH8 Hamiltonian and the differences between them and the respective non-relativistic results given in Tables I and II. All energies are in eV. T and S refer to triplet and singlet couplings of two core holes created on different atomic sites, respectively.

Molecule	State	Ionization Potential	Difference
CO	$C1s^{-1}$	296.446	0.088
	$O1s^{-1}$	543.166	0.346
	$C1s^{-2}$	664.661	0.243
	$O1s^{-2}$	1177.408	0.847
	$C1s^{-1}O1s^{-1}$, S	855.176	0.433
	$C1s^{-1}O1s^{-1}$, T	855.632	0.432
BF	$B1s^{-1}$	201.758	0.034
	$F1s^{-1}$	696.500	0.585
	$B1s^{-2}$	465.425	0.102
	$F1s^{-2}$	1497.177	1.368
	$B1s^{-1}F1s^{-1}$, S	911.187	0.619
	$B1s^{-1}F1s^{-1}$, T	911.297	0.619

TABLE VI. Basis set dependence of the CASSCF single and double core hole ionization potentials. All energies are in eV. T and S refer to triplet and singlet couplings of two core holes created on different atomic sites, respectively.

Molecule	State	cc-pVDZ	cc-pVTZ	cc-pCVTZ	cc-pVQZ
C ₂ H ₂	C1 g^{-1}	293.262	292.202	292.111	291.728
	C1 u^{-1}	293.172	292.111	292.020	291.634
	C1 s^{-2}	658.167	650.228	649.412	649.711
	C ₁ 1 s^{-1} C ₂ 1 s^{-1} , S	598.350	594.590	594.337	593.908
	C ₁ 1 s^{-1} C ₂ 1 s^{-1} , T	598.853	595.197	594.971	594.592
CO	C1 s^{-1}	298.062	296.358	296.239	296.229
	O1 s^{-1}	544.881	542.820	542.611	542.559
	C1 s^{-2}	672.908	664.418	663.663	663.632
	O1 s^{-2}	1184.846	1176.561	1175.469	1175.373
	C1 s^{-1} O1 s^{-1} , S	859.146	854.743	854.452	854.425
	C1 s^{-1} O1 s^{-1} , T	859.491	855.200	854.931	854.905

TABLE VII. Effect of dynamic correlations examined by the CI calculation. All energies are in eV.

Molecule	State	CASSCF	CI
C_2H_2	$\text{C}1g^{-1}$	292.202	292.216
	$\text{C}1u^{-1}$	292.111	292.127
	$\text{C}1s^{-2}$	650.228	650.586
	$\text{C}_11s^{-1}\text{C}_21s^{-1}$, S	594.590	594.728
	$\text{C}_11s^{-1}\text{C}_21s^{-1}$, T	595.197	595.319
CO	$\text{C}1s^{-1}$	296.358	296.386
	$\text{O}1s^{-1}$	542.820	543.070
	$\text{C}1s^{-2}$	664.418	664.658
	$\text{O}1s^{-2}$	1176.561	1177.096
	$\text{C}1s^{-1}\text{O}1s^{-1}$, S	854.743	854.833
	$\text{C}1s^{-1}\text{O}1s^{-1}$, T	855.200	855.276

FIG. 1. (Color online). Schematic picture of x-ray two-photon photoelectron spectroscopy (XTPPS) and x-ray two-photon-induced Auger electron spectroscopy (XTPAES). See text for explanations. In this picture it is assumed that the second photon is absorbed before Auger decay takes place and that one core hole decays much faster than the other. In reality all processes overlap.

FIG. 2. (a) The energy difference $\Delta E1(S^{-2}) = DIP(S^{-1}, S^{-1}) - [IP(S^{-1}) + IP(S^{-1})]$ as a function of the atomic number Z of the atom with the core orbital S ; (b) The generalized relaxation energy $RC(S^{-1})$ calculated by means of Eq. (15) as a function of Z .

FIG. 3. The ratio $n = RC(S^{-1}, S^{-1})/RC(S^{-1})$ as a function of the atomic number Z of the atom with the core orbital S .

FIG. 4. (a) The energy difference $\Delta E2(S_i^{-1}, S_j^{-1}) = DIP(S_i^{-1}, S_j^{-1}) - [IP(S_i^{-1}) + IP(S_j^{-1})]$ as a function of the inverse distance r between the atoms with the core orbitals S_i and S_j ; (b) The interatomic generalized relaxation energy $IRC(S_i^{-1}, S_j^{-1})$ calculated by means of Eq. (16) as a function of r .

FIG. 5. Differences between the valence electron density distributions of the ground and double core hole states: (a) $C_1 1s^{-2}$ of C_2H_4 ; (b) $C_1 1s^{-1}C_2 1s^{-1}$ (singlet) of C_2H_4 ; (c) $O 1s^{-2}$ of CO

FIG. 6. The two-electron integral V_{SSSS} as a function of the atomic number Z of the atom with the core orbital S . The results extracted from the *ab initio* calculations (filled circles) are compared with those calculated by means of Eq. (10) (dotted curve). A linear fit of the *ab initio* results is also shown (dashed curve).

FIGURE CAPTIONS











